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Aggregation of colloidal particles in a non-equilibrium backflow induced by electrically-driven reorientation of the nematic liquid crystal

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ABSTRACT

We study the dynamics of anisotropic aggregation of spherical colloidal particles with dipolar interactions, dispersed in a nematic liquid crystal. The director is perpendicular to the surface of spheres so that each particle creates a dipolar distortion when placed in a uniformly aligned planar nematic slab. A backflow of the nematic caused by periodic voltage pulses, propels the spheres in a bidirectional fashion, so that the dipoles of one polarity move in the direction antiparallel to the dipoles of opposite polarity. The dipoles experience inelastic collisions, head to tail and head to head. The head-to-tail collisions of similarly oriented dipoles result in linear aggregation parallel to the backflow, while the head-to-head collisions lead to aggregation in a transversal direction. The two flows are separated by an impact parameter that controls the frequency of head-to-head collisions and thus the resulting shape of aggregates, their anisotropy and fractal dimension. We discuss in detail the numerous forces of elastic, electrophoretic and dielectrophoretic nature, as well as gravity forces, acting on colloidal spheres suspended in an electrically driven slab of a nematic liquid crystal. The proposed "nematic collider" offers opportunities in the quantitative studies of non-equilibrium processes such as anisotropic aggregation and jamming, as well as in the development of systems capable of self-assembly through anisotropic interactions of the building units.

1. Introduction

Behavior of colloidal particles dispersed in a fluid medium is of a significant research interest. Typically, the dispersive medium is an isotropic fluid and the particles interact through the central forces with a magnitude that depends only on the distance r between them but not on the direction in space. The concept of central forces is often sufficient to describe the static and dynamic properties of spherical particles, for example, formation of colloidal crystals in a system of closely packed spheres. When the interactions depend not only on the distance but also on the direction in space, the system becomes much harder to study but also more promising in terms of potential applications. The non-central interactions are of a great promise in designing new materials [1], as demonstrated by studies of magnetic dipolar colloids [2–5], Janus particles [6–8], colloids with electric [9–13] and magnetic [14,15] field-induced dipoles. Anisotropy of interactions is reflected in aggregation geometry. For example, diffusion limited aggregation of spheres with central forces produces structures with fractal dimension d_f between 1 and 2 in two dimensions (2D) and between 1 and 3 in 3D, see, e.g., [16]. Once dipolar interactions are switched on, d_f reduces dramatically, down to 1 in both 2D and 3D, reflecting head-to-tail chaining [2,14,15].

Liquid crystals (LCs) and, in particular, nematic liquid crystals (NLCs), represent a unique dispersive environment in which the anisotropy of colloidal interactions is created by the host medium itself rather than through the broken symmetry of the particle. In the NLC, the average orientation of anisotropic molecules is specified by a non-polar unit vector $\hat{\mathbf{n}}$ with the property $\hat{\mathbf{n}} \equiv -\hat{\mathbf{n}}$. Molecular interactions are anisotropic in the bulk of NLC and also at an interface between a NLC and an adjacent medium [16]. The direction of surface alignment established by the anisotropic molecular interactions at the interface is called an "easy axis". In this work, we are dealing with particles at which the easy axis is everywhere perpendicular to the surface. Locally, the director around the spherical particle tends to form a radially symmetric structure, reminiscent of a radial point defect-hedgehog with a topological charge 1 [16]. If such a particle is placed into a uniformly aligned flat NLC slab, in which the director is fixed, $\hat{\mathbf{n}}_0(\mathbf{r}) = (1, 0, 0)$, say by a unidirectional rubbing of the bounding plates, then the matching between the conflicting director fields is achieved through the introduction of an additional defect, a hyperbolic hedgehog (to which one can assign a topological charge -1 so that the total topological charge in the system is preserved) [17]. For tangential "easy axis" at the spherical surface, the director field around the sphere is of quadrupolar symmetry with two surface point defects-boojums [17]. The interactions can be thus of a dipolar or quadrupolar type, depending on symmetry of the director configuration around the particles [17–21]. These non-centrosymmetric interactions lead to strongly anisotropic aggregates of spherical particles in a NLC host, such as linear chains arranged parallel to

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the direction of $\hat{\mathbf{n}}_0$ (the case of radial boundary conditions) [18–20] or at some angle to $\hat{\mathbf{n}}_0$ (for the tangential conditions) [20,21].

In regular isotropic fluids, gravity causes dispersed particles to sediment, i.e., to drop to the bottom of the container (when the particle's density is higher than that of the fluid). The effect is detrimental to the development of three-dimensional assembly techniques and to an efficient transport of particles. The physics of particles dispersed in a LC is entirely different. It includes the effect of elastically-mediated levitation [22,23] that allows one to avoid sedimentation completely. The physical mechanism is simple and is based on the fact that the distorted director configuration around the particle causes anisotropic interactions with the bounding surfaces. Suppose that a particle moves towards the bounding plate, say, under the action of gravity. When the associated distorted NLC region moves close to a flat surface with a certain uniform "easy axis", the director gradients in most cases become stronger and the NLC elasticity leads to a "lifting" force that keeps the particle "levitating" at some distance away from the substrate. The height of levitation, determined by the balance of the elastic and gravitational forces is in the range of microns and tens of microns for typical NLCs and for spheres of a few micron size [22,23]. The elastic forces are significant and scale with the radius of sphere as R^4 (for the dipole-type distortions), thus overcoming the gravity force $\sim R^3$ is easier for larger particles than for the smaller ones [23].

The director orientation in a NLC can be easily controlled by the electric field, through the anisotropy of dielectric permittivity, an effect widely used in modern displays. This brings an opportunity for the electrically controlled manipulation of particles. In a regular fluid, the classic means of moving a particle around are either an electrophoretic effect (when the particle is electrically charged) or a dielectrophoretic effect (in a non-uniform electric field), see, for example, [24]. In the NLC, the spectrum of opportunities is much wider. First of all, the classic mechanisms acquire new facets. For example, when an electrophoresis is performed in a NLC (as opposed to an isotropic fluid), the effect becomes strongly nonlinear, with the electrophoretic velocity scaling with the applied field as E^2 [25] rather than linearly, as in the celebrated formula derived by Smoluchowski [26]. In dielectrophoretic manipulation with the involvement of NLC, the gradients of the electric field can be created not only by the special geometry of electrodes, but also through the spatial nonuniformity of the dielectric permittivity, associated with the director reorientations, as briefly alluded to in Ref. [23] and considered in a greater detail in Ref. [27] and in this work. Second, the director-electric field coupling through the dielectric anisotropy and the anisotropic mobility of charge carriers allows for new effects that are in principle impossible in isotropic molecular fluids. One of these is particle transport by the so-called backflow [22,28], generated when the applied electric field reorients the director [29]. In the future, the new mechanisms of particle manipulation in NLCs may result in practical applications, such as self-assembly of complex structures through anisotropic interactions mediated by LC elasticity, particles sorting, electrically-driven LC microfluidic devices, new types of electrophoretic displays, etc. However, it is already clear that the colloidal dispersions in a NLC subject to an electric field can also be a rich field for basic studies of assembly, transport and nonequilibrium phenomena, offering experimental realization of situations one considers in diffusive systems [30–34], traffic phenomena [35], pedestrian dynamics [36], etc.

In this paper, we extend our previous study [22,23] of an electric field-induced backflow and dynamics of spherical colloidal particles to the case when the number density of colloidal particles is high and leads to their frequent inelastic collisions and aggregation. A brief account of the main results of this work has been presented in Ref. [27]. The colloidal particles in question are spheres with perpendicular surface anchoring that create dipolar distortions around themselves. We chose the direction of this dipole from the hyperbolic hedgehog towards the sphere. Depending on the location of the hyperbolic hedgehog, on the left hand side or the right hand side of the sphere, the elastic dipole $\mathbf{p}=(p_x,0,0)$ can be directed in one of the two opposite directions, $p_x>0$ or $p_x<0$; these states, which we will also label with symbols ">" and "<" for shortness, are of equal probability. Once the direction of $\mathbf{p}$ around the sphere is established at the stage of sample preparation, it cannot be changed as the states are separated by a large energy barrier. The aggregation of particles with $p_x>0$ and $p_x<0$ is controlled in a specially designed "nematic collider". The two types of particles, ">" and "<" are forced into two types of non-diffusive pair-wise collisions, "$\gg$" (or "$\ll$") and "$\substack{>\\<}$" by a bidirectional NLC flow driven by periodic voltage pulses. Particles ">" move unidirectionally in one plane, while particles "<" move in an antiparallel direction, located at an impact distance b from the first plane. The inelastic collisions result in anisotropic aggregates, Fig. 1. Two different scenarios of collisions lead to particles aggregation along two different directions, parallel to $\hat{\mathbf{n}}_0$ for the "$\gg$" and "$\ll$" collisions and perpendicular to $\hat{\mathbf{n}}_0$ for the "$\substack{>\\<}$" collisions. We demonstrate that the scenario and geometry of particle aggregation is controlled by the impact parameter b. In the nematic collider, the value of b represents a measure of the distance between the two backflow streams carrying the "<" and ">" particles. It is controlled by simply changing the NLC cell thickness. By decreasing b and enhancing the probability of the head-to-head collisions, one increases the fractal dimension d_f of the ensuing aggregates well above the value of 1 characteristic of dipolar systems with diffusion driven aggregation [2,9–15]. Expanding the original brief account of experimental data reported in Ref. [27], we discuss in detail the physical mechanisms that control the dynamics, interactions and anisotropic assembly of the colloidal particles driven by backflow.

The article is organized as follows. Section 2 describes the experimental findings of colloidal aggregation. Section 3 discusses the dynamics of particles aggregation and quantifies the fractal character of colloidal clustering. Section 4 discusses the forces acting on moving particles. Section 5 presents the conclusions.

2. Experiment

We studied the NLC E7 (EM Industries) with dispersed spherical silica particles of diameter $2R\approx(4.1\pm0.4)\mu\text{m}$ (Bangs Laboratories, Inc.) at concentrations ~0.5–4 wt.%. The surface of particles was modified by *octadecyltrichlorosilane* (Sigma-Aldrich) to promote normal boundary conditions of director at particle's surface. To modify the surface we dispersed colloidal spheres in the mixture of hexane and octadecyltrichlorosilane (1 wt.%). After heating and evaporation of hexane, the particles were dispersed in E7. The cells were formed by glass plates, with the inner surfaces covered with transparent indium tin oxide (ITO) electrodes and rubbed polyimide PI2555 (Microsystems) layers. The unidirectionally rubbed plates were assembled in an antiparallel fashion to assure a homogeneously aligned NLC, Fig. 2a. The rubbing resulted in a small (1–2°) pretilt of the director $\hat{\mathbf{n}}_0$ with respect to the plane of the cell, which facilitated the experiments, as the pretilt angle eliminated the degeneracy of "clockwise" and "anticlockwise" directions of director reorientation. The cells were filled with E7 by capillary effect. The cells thickness d was varied by using different spacers separating the plates; the most effective control of impact parameter was observed for the cells thicknesses $6\mu\text{m}\le d\le 10\mu\text{m}$. Polarizing microscopy (PM) studies revealed a formation of hyperbolic hedgehogs accompanying each colloidal particle, thus confirming normal director orientation at particles surface.

When there is no electric field, the colloidal particles are distributed randomly at approximately the same vertical z coordinate, as confirmed by fluorescence confocal polarization microscopy (FCPM) [37], Figs. 1a, 2a, 3b,d. Since concentration of the particles in the cell is rather high, they interact, tending to aggregate and form anisotropic clusters even when there are no electrically induced flows. This is